**DETECTION OF ABIOTIC METHANE IN TERRESTRIAL CONTINENTAL HYDROTHERMAL SYSTEMS: IMPLICATIONS FOR METHANE ON MARS.**

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Introduction: The recent detection of methane in the Martian atmosphere [*1, 2*] and the possibility that its origin could be attributed to biological activity, have highlighted the importance of understanding the mechanisms of methane formation and its usefulness as a biomarker.

Much debate has centered on the source of the methane in hydrothermal fluids [*3-5*], whether it is formed biologically by microorganisms, diagenetically through the decomposition of sedimentary organic matter, or inorganically via reduction of CO_2 at high temperatures. Ongoing research has now shown that much of the methane present in sea-floor hydrothermal systems is probably formed through inorganic CO_2 reduction processes at very high temperatures (>400°C) [*6, 7*]. Experimental results have indicated that methane might form inorganically at temperatures lower still [*8-10*], however these results remain controversial [*11*]. Currently, methane in continental hydrothermal systems is thought to be formed mainly through the breakdown of sedimentary organic matter and carbon isotope equilibrium between CO_2 and CH_4 is thought to be rarely present if at all [*12, 13*].

Based on isotopic measurements of CO_2 and CH_4 in two continental hydrothermal systems, we suggest that carbon isotope equilibration exists at temperatures as low as 155°C. This would indicate that methane is forming through abiotic CO_2 reduction at lower temperatures than previously thought and could bolster arguments for an abiotic origin of the methane detected in the martian atmosphere.

Results: Preliminary measurements of relative gas abundance and isotopic composition have been performed on gases collected from two terrestrial hot spring environments: Great Boiling Springs, NV (GBS), part of the Gerlach Thermal Area, located ~2 km WNW of Gerlach NV, and Surprise Valley Hot Springs, CA (SVHS), located ~ 5 km east of Cedarville, CA. Carbon dioxide and CH_4 gas was sampled non-destructively at these hot springs and analyzed for
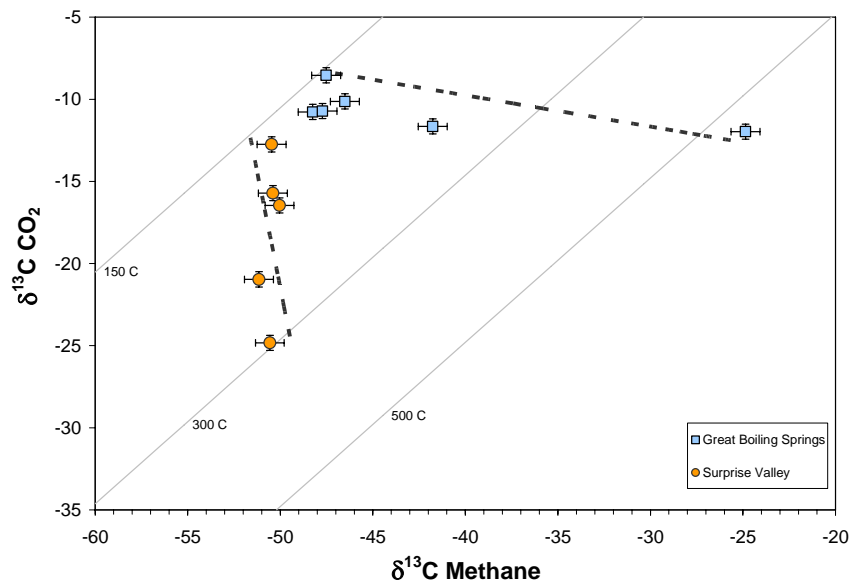
Figure 1. Carbon isotope data from two different hot spring systems. The light solid lines represent equilibrium fractionation using data from Horita (1999) at the temperatures 150°, 300°, and 500°C. The dashed lines represent calculated carbon isotope values from the model explained in the text.

C isotope composition. The $\delta^{13}C$ values for CO_2 ranged from -12.0 to -8.5‰ for GBS, and from -24.8 to -12.8‰ for SVHS. The $\delta^{13}C$ values for CH_4 ranged from -48.3 to -24.83‰ for GBS, and from -51.2 to -50.0‰ for SVHS. The ratio of CH_4/CO_2 gas abundances from each field site were distinct with the GBS field were primarily composed of CO_2 while SVHS was dominated by CH_4.

Discussion: Stable isotope systems are very sensitive to temperature differences which can cause large changes in the isotopic fractionation between two substances. In a closed system, the mass balance of the isotopic constituents plays an important role in how the isotopic composition of each species changes with temperature. For example in a system dominated by CO_2 over CH_4, any changes in the carbon isotope fractionation between CO_2 and CH_4 would result in significant changes to the $\delta^{13}C$ of CH_4 and minimal changes to the $\delta^{13}C$ of the CO_2. This is because the amount of carbon in methane is not sufficient to significantly affect the overwhelming amount of carbon in CO_2. The data from SVHS, and GBS (Fig. 1) suggest that a mass balance relationship is driving the variation because the methane dominated SVHS gases show very little variation in $\delta^{13}C$ of methane and large variations in the $\delta^{13}C$ of the CO_2, while CO_2 domi-

nated GBS gases show large variations in the $\delta^{13}C$ of the methane with very small variations in $\delta^{13}C$ of CO_2.

A carbon isotope mass balance model was constructed to explain these data. This model calculates the equilibrium carbon isotope composition of CH_4 and CO_2 according to the set of two equations:

(1) $\delta^{13}C_{TC} = X_{CH4} * \delta^{13}C_{CH4} + X_{CO2} * \delta^{13}C_{CO2}$
(2) $\delta^{13}C_{CO2} - \delta^{13}C_{CH4} = 10^3 * \ln \alpha_{CO2-CH4}$

X_{CH4} and X_{CO2} are the relative abundance of each species in the gas sample, $\delta^{13}C_{TC}$ is the carbon isotope composition of total carbon, $\alpha_{CO2-CH4}$ is the carbon isotope fractionation factor between CO_2 and CH_4, and $\delta^{13}C_{CH4}$ and $\delta^{13}C_{CO2}$ are the carbon isotope compositions of each species. The model is a series of two equations with two unknowns. The unknowns are the $\delta^{13}C$ of both CH_4 and CO_2. X_{CH4} and X_{CO2} are measured, $\delta^{13}C_{TC}$ is calculated from the average X_{CH4}, X_{CO2}, and average $\delta^{13}C$ values, and $\alpha_{CO2-CH4}$ is known at a given temperature [8]. The results of these calculations are a set of $\delta^{13}C$ values for CH_4 and CO_2 over a range of temperatures that appear as a straight dashed line on the $\delta^{13}C_{CH4}$ vs. $\delta^{13}C_{CO2}$ plot (Fig. 1). The slope of this line is determined by the relative abundance of CH_4 to CO_2 in the system, the length of the line is determined by the range of temperatures used in the calculation, and the absolute position of the line in X-Y space is determined by the $\delta^{13}C$ of total carbon.

The model assumes that the isotopic changes are due to changes in temperature while equilibrium is maintained between CO_2 and CH_4, and that no new gases are added or lost from the reservoir. At high CH_4/CO_2 ratio, as in the SVHS system, changes in temperature result in large changes in the $\delta^{13}C$ value of CO_2 but small changes in $\delta^{13}C$ value of CH_4, while at low CH_4/CO_2, as in the case in the GBS system, changes in temperature result in large changes in the $\delta^{13}C$ values of CH_4 with only minor changes to the $\delta^{13}C$ values of CO_2.

The agreement between the slope of the modeled compositions (dotted line in Fig. 1) and the slope of the actual isotope data (data points in Fig. 1) suggests that the relative gas abundances are correlated with the carbon isotope composition of the gases via mass balance equilibrium relationships. The way in which the model calculates $\delta^{13}C_{TC}$ ensures that the modeled compositions will always be in the vicinity of the measured points. However, it is the slope of the line which dictates the agreement between the model and the measured data points. Thus for both spring systems, the data agree well with the model which suggests that carbon isotope equilibrium was established.

Calculated carbon isotope equilibrium temperatures range between 155 - 590°C [14] with a majority of the points clustering between 150 – 300°C which is very reasonable for the deeper portions of a hydrothermal system. Any later alteration to the system through post formational processes would be extremely unlikely to reproduce these relationships, and we deem it unlikely that these observed relationships are the result of a fortuitous mixture, or post-formational process that mimics isotope equilibrium. In addition, all of the samples indicate temperatures above 155°C, which is well above the accepted limit for the viability of life (~120°C) and therefore excludes the possibility that methane formed directly from the action of microorganisms.

The assumptions and constraints posed by the carbon isotope mass-balance model suggest a very particular set of geologic conditions. The model assumes a closed system at a variety of temperatures which is consistent with the following scenario: (A) at the deepest portions of the hydrothermal system, the relative abundance of CH_4 to CO_2 was fixed; (B) as this packet of gas migrated toward the surface it cooled and split up among different fracture pathways; (C) each pathway provided a slightly different temperature profile and gases re-equilibrated at lower temperatures in many cases while retaining their basic CH_4/CO_2 ratio; (D) different hot spring pools at the surface then sample gases from different temperature profiles, with some sampling deeper, higher temperature reservoirs while others sample cooler, more shallow reservoirs.

These results indicate that abiotic formation of methane in terrestrial continental hydrothermal systems may be more common than previously thought and may also be common in deep hydrothermal systems on Mars. This supports previous work that has proposed an abiotic source for methane in the martian atmosphere [15, 16].

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